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Combined Techniques of Raman Spectroscopy and Synchrotron X-ray Diffraction for *in-situ* Studies of Isotactic Polypropylene Fibers during Tensile Deformation

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Beamline(s): X27C

Introduction: Raman spectroscopy is a technique to study the vibrational spectra of the material, often using a coherent, intense laser beam as the probe. Using synchrotron X-rays, time-resolved wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) have been used routinely in recent years to obtain dynamic structural and morphological information during polymer processing, such as stretching, spinning and shearing [1-3]. However, these techniques are generally not sensitive to the change in the amorphous phase. Although it has been mentioned that the combination of Raman spectroscopy with synchrotron X-ray techniques (SAXS and WAXD) could be a powerful tool to study the *in-situ* structural and morphological change of polymers undergoing physical phase transitions or/and chemical reactions [4], the detailed experimental setup and data have not been available, which is the objective of this study.

In the present work, we have demonstrated a combined system of Raman spectroscopy and synchrotron WAXD, which was assembled at the X27C beamline of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). This system exhibited the unique advantages that can provide complementary information on the structure and morphology of the polymers. For the first time, the *in-situ* Raman spectra and 2D WAXD patterns have been obtained simultaneously during the stretching of a semicrystalline iPP fiber.

Methods and Materials: Fig.1 shows a schematic diagram of the setup combining Raman spectroscopy and synchrotron WAXD with the stretching apparatus (modified Instron 4410). In order to obtain the dynamic information during the deformation of fibers, the Renishaw fiber-optic probe was modified and then coupled to the Raman spectrometer. The probe head was equipped with an Olympus long working distance objective, which had a numerical aperture of 0.4. Considering that the focus was continuously being changed during stretching, the probe was placed on a translational stage that could be remotely controlled, enabling the focus on the fiber to be adjusted accordingly during deformation. The distance between the thermostated probe objective and the fiber was about 13 mm. The isotactic polypropylene (iPP) fibers were provided by Basell USA. The stretching experiment was performed at room temperatures. The chosen stretching speed was 4 mm/min. After having reached the desired stretch ratio, the fiber was held for about 2 min for simultaneous collection of both WAXD image and Raman spectrum and was then subjected to the next stretch ratio. 2D WAXD patterns were recorded by using a CCD X-ray detector (MAR-USA) at X27C beam line at National Synchrotron Light Source, Brookhaven National Laboratory. The distance between the detector and the sample for WAXD was 158.0 mm, which was calibrated using an Al_2O_3 standard. All the Raman spectra were acquired in the 'extended' mode with 1200 (NIR/VIS) grating. The spectral range covered 200 ~ 2000 cm^{-1} with a spectral resolution of about 7 cm^{-1}. The stretching experiments were repeated with different combinations of polarizer and analyzer directions.

Results: 2D WAXD results showed that α-form iPP crystals were converted into the mesophase upon stretching at room temperature. Corresponding polarized Raman spectra (ZZ spectra at different extension ratios with polarizer and analyzer being set parallel to the fiber direction were shown in Fig.2) showed that characteristic Raman bands of crystal (898, 945, 1002 cm^{-1}) became weaker or disappeared during the transition from the crystal phase to the mesophase. Meanwhile, the fingerprints of the helical structure (around 1333 cm^{-1}) still existed, indicating that the helix conformation remained in the mesophase, which was consistent with the WAXD results. The Raman band at 812 cm^{-1} did not disappear in the mesophase implying that the differences observed between crystal and mesophase of iPP were due to the packing defects in the mesophase, such as the random assembly of helical hands, rather than the conformational deviations from the (…TGTG…) sequence. The Raman intensity ratio (I812/I843) was found to be suitable to characterize the orientation change of the fiber qualitatively.

Conclusions: The combined technique of Raman spectroscopy and synchrotron WAXD was successfully demonstrated to study the *in-situ* structural changes during isotactic polypropylene fiber deformation. 2D WAXD results showed that α-form iPP crystals were converted into the mesophase upon stretching at room temperature. Corresponding Raman spectra suggested that the differences observed between crystal and mesophase of iPP were due to the packing defects in the mesophase, rather than the conformational deviations from the (…TGTG…) sequence.

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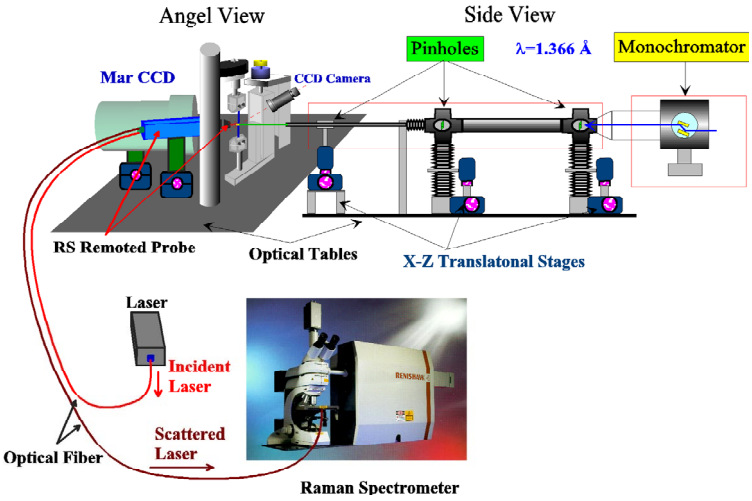

Figure 1. Schematic diagram of the setup combining Raman spectroscopy and synchrotron WAXD with the stretching apparatus

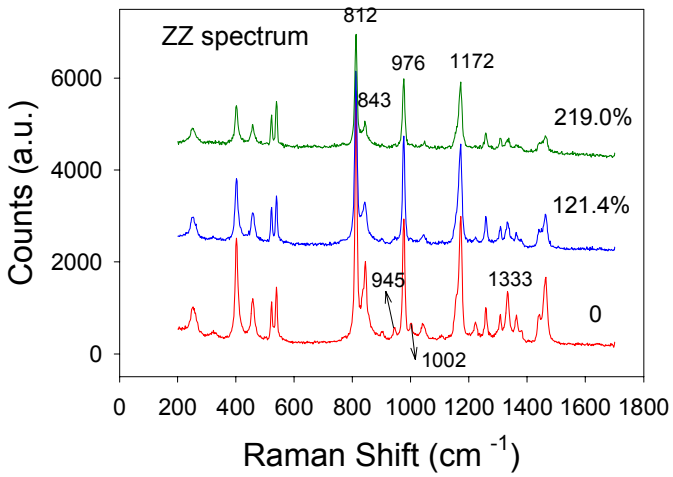

Figure 2. One-dimensional equatorial scattered intensity, obtained by averaging ±5º sectors on the equator of 2D scattering patterns, of PBO filament with a spin-draw-ratio (SDR) of ~2.0 before coagulation and at different coagulation times.